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Review on Low Cost Adsorbents for Desulphurization of Liquid Fuels

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ABSTRACT

Adsorptive desulphurization method used for removal of sulphur from diesel and other liquid fuels.The presence of sulphur compounds in liquid fuels is always objectionable in the world due to their harmful effects on combustion.The various sulphur compounds generally found in diesel oil are mercaptants, sulfides and aromatic ring structured compounds thiophenes. In this paper we studies the use of various adsorbents which lower the overall percentage of sulphur level from diesel. Desulphurization separates sulphur from fuel, yielding elemental sulphur fuel contains sulphur in a more concentrated solid or liquid form. Sulphur in liquid fuels is present in thiols ,mercaptants, sulfides, disulfides ,thiophenes and derivatives. The desulphurization process is essentially adsorptive process.In present work; report on the application of different adsorbents for desulphurization of various petroleum fractions.

Keywords : Desulphurization, Adsorption Adsorbents, Liquid Fuels, Sulphur

I. INTRODUCTION

For improving air quality sulphur content should be decreases from liquid fuels.The presence of sulphur in liquid fuels creates pollution. The present work gives the knowledge about different types of adsorbents used for desulphurization of liquid fuels.In the current study desulphurization of liquid fuel carried out using different variety of adsorbents.The study is conducted for elimination and reduction of the percentage of sulphur in liquid fuel.Adsorptive desulphurization is commonly used for sulphur removal from fuels. And it is one of the easy and fast methods for sulphur removal from liquid fuel. Sulphur oxides are produced from the burning of fuels which mainly contains sulphur .Emission of sulphur cause serious impacts on human health and the environment.This paper summerise various adsorbents available for desulphurization techniques. The sulphur problem is becoming more serious in general, particularly for diesel fuels as the regulated sulphur content.The desulphurization process is essentially an adsorptive process. Activated carbons are widely used as adsorbents.The performances of several kinds of commercial adsorbents used in desulphurization is studied.Presence of sulphur compounds in petroleum is always harmful due to their process and their process and environmental problems.

II. DIFFERENT ADSORBENTS FOR REMOVAL OF SULPHUR METHODS AND MATERIAL

A) Date palm kernel powder:

Adsorption Process of Sulfur Removal from Diesel Oil using Sorbent Materials has been studied by Isam A.and Al Zubaidy [1] They used Date palm kernel powder for desulphurization process for diesel fuel. Sulphur content was measured using Spectro iQ ii X-ray fluorescence analyzer and other physical properties were conducted according to ASTM standard methods.author varied amount of commercial activated carbon between 0-10%. The sulfur content was plotted vs. amount of commercial activated carbon and curve showed continuous decrease of sulfur content.They showed that Carbonized material from date palm kernel was also used but without activation for desulfurization process of diesel fuel and able to reduce sulfur content by 34.15%

with the addition of 6% by mass sorbent material. Also it was found that sulfur content was reduced from 410 ppm to 251 ppm using 5% adsorbent material and further reduction and up to184.6 ppm using 10% sorbent material.

B) Neem leaves powder:

Desulphurization of diesel by using low cost adsorbent was studied by Gaurav Daware and Akshay Kulkarni[2].They were used Neem leaves as adsorbent for sulphur removal from diesel. They were carried out experiments at 283, 288 and 293K with different initial concentrations. and used UV-visible spectrophotometer for analysis of sulphur. They were carried out experiments for Effect of adsorbent dose, Effect of initial concentration and time, Effect of initial concentration and temperatures .Authors were observed that nature of graph between sulphur content vs. time is decreasing.They were carried out number of experimental runs for determination of residual sulphur concentration in the solution with time (t) during the initial sorption period. The sorption kinetics was studied by using the pseudo-first-order and pseudo-second-order kinetic model to fit the experimental kinetic data.

C) Nano copper oxide (CuO)

Khodadadia and M. Torabi[3] studied adsorptive desulfurization of diesel fuel with nano copper oxide (CuO).They showed that the CuO nano particle could be used as adsorbent for the desulfurization of liquid fuels. They were used petrotest calorimetric bomb C5000 according to ASTM D-1266 for sulphur analysis and carried out Batch experiment for determination of the kinetic models. They conducted the experiments for effect of temperature, effect of contact time, effect of adsorbent does, effect of agitation.They conducted the batch experiments using CuO nano particle as sorbent. To test the effect of temperature and agitating rate and CuO nanoparticle concentration. It was observed that the equilibrium adsorption data followed freundlich isotherm. The research was also carried out for the effect of temperature, effect of contact time, effect of adsorbent does and effect of agitation.

D) Manganese Dioxide:

Kinetics Analysis and Dosage Effects of Manganese Dioxide Adsorbent on Desulphurization of Crude Oil was studied by A. A. Adeyi and L. T. Popoola[4].The research was particularly on the effects of Manganese Dioxide Adsorbent on Desulphurization of Crude Oil In batched experiments, manganese dioxide was applied to adsorb sulphur in the crude oil. This research work explored the influence of contact time and doses of adsorbent. The kinetics analysis of sulphur uptake from crude oil sample was executed using pseudo-first-order and second-order rate equations. Authors examined the kinetics analysis and dosage effects of manganese dioxide adsorbent on desulphurization of crude oil and noted that the activated manganese dioxide proved to be efficient during the adsorption of sulphur compounds from crude oil. And was found that desulphurization efficiency was found to increase with increasing sorbent dose and contact time. They carried out experiments for the effect of the contact time and adsorption of sulphur was measured at constant sulphur concentration for six different contact times from 1 to 6 hours at room temperature and fixed amount of AM. They also studied effect of Dose on Desulphurized Crude Oil to control both availability and accessibility of adsorption sites .The effect of adsorbent dose was studied at room temperature (30 0C) by varying the sorbent amounts from 1 g to 5 g.

E) Black Liquor:

M.S.Patil and Y.C.Bhattacharyulu[5] was carried out desulphurization of hydrocarbon liquid fuels by adsorption .Authors was carried out experiments for Sorption of sulfur onto activated carbons by batch reactor And activated carbon was prepared from black liquor. It was found that intra-particle diffusion resistance has been overcome due to stirring. The experimental data obtained obeys Langmuir adsorption isotherm model.authors was observed that variation in parameters like Mercaptan feed conc., Stirring speed, Particle size , temperature and effect of solvent. The analysis of product was done by determining the conc. of mercaptan by silver nitrate method recommended by ASTM. The research is also carried out for the uptake capacity of various carbons the uptake capacities of laboratory prepared carbons were compared with the uptake capacities of commercial carbons in removing sulfur from benzene. Kinetic runs were carried out at different conc.at different stirring speeds for each conc.

F) Mineral Clays

Desulphurization of liquid fuels by selective adsorption through mineral clays as adsorbents was studied by M.Shakirullah and W.ahmad. Authors was studied adsorptive desulphurization of Jhal Magsi Crude oil, kerosene oil and diesel oil carried out using zeolitic clays (montmorollinite, vermiculite, palygorskite and kaolinite), Charcoal and ion exchange resin as adsorbents for the sulphur compounds at 40 ^{o}C for different time intervals i.e. one hour, three hours and six hours. They compared the desulphurization activity of the clay with the charcoal, ion exchange resins and with each other.They were used SEM and EDX analysis methods for characterization of surface area.Adsorption was investigated at different duration of time i.e. 1hr, 3hrs and 6 hrs. The sample was filtered and analyzed for sulphur contents. The mineral clays were characterized by various analytical methods to know its surface area, morphology and mineralogical composition.The fractions obtained were analyzed for their various physicochemical properties, employing the standard procedures of ASTM an API.

G) Rice Husk

Yoshie Shimizu and Seiji Kumagai was carried out desulphurization of kerosene by using rice husk activated carbon. They used Japanese rice husk samples were obtained by rice threshing performed in autumn of 2002, 2003 and 2004. for removal of sulphur from kerosene. They studied the evaluation of capacities of rice husk activated carbons to adsorb refractory sulfur compounds of dibenzothiophenes by correlating with their textural and chemical characteristics.The DBTs adsorption capacity of the rice husk activated carbon (RHAC) in commercial kerosene was evaluated, with a correlation with textural and chemical characteristics. A micro-porous activated carbon fiber (ACF) was also tested for a comparison with the RHAC. A huge quantity of rice husk (ca. 3 million tons) is produced every year as agricultural waste in Japan. In the present study, rice husk was converted into activated carbon intended for a removal of DBTs from kerosene by employing CO2 gas activation method. Authors studied the textural and chemical characteristics of the obtained RHACs as well as the ACF having much larger S_{BET} and V_t were evaluated in order to correlate their DBTs adsorption capacity in the kerosene.

H) Chloramine T and Polymer supported Imidation agent:

Neran K. Ibrahim and Najat J. Saleh was desulfurization of Light Diesel Fuel Using Chloramine T and Polymer Supported Imidation Agent. Authors was focuses on a novel desulfurization process for light diesel fuel based on the chemical adsorption of sulfur compounds on a polymer-supported imidation agent (Sodium N-chloro-polystyrene sulfonamide, PI) at ambient conditions. The activity of the synthesized PI was investigated at first with respect to the removal of DBT from model light oil corresponding to 500 ppm sulfur content.They were studied the effects of initial sulfur concentration in commercial oil and the sorbent dose at time equal to 40 hr on the desulfurization efficiency and the results indicate that the removal efficiency increased with decreasing sulfur concentration and increasing sorbent dose and they concluded that The present process was found to be also effective for the desulfurization of actual light diesel oil the sulfur concentration was decreased from 1900 ppm to about 180 ppm .Authors were carried out experiments for finding out desulfurization efficiency and was found to be increasing on increasing sorbent dose and reducing initial sulfur concentration in diesel oil. Deep desulfurization level could be successfully achieved for Beji diesel oil using PI at ambient conditions and at sorbent dose FT-IR technique was used to identify the PI structure and it was found to be identical with the standard. The DBT concentration in model light oil was analyzed by Gas Chromatography while the sulfur concentration of actual oil was determined by x-ray fluorescence analyzer, and IR spectra were measured using FT-IR infrared spectrophotometer on KBr disks. They concluded that a complete removal of sulfur compounds from model light oil using chloramine T and PI was achieved after 4.5 hr and 8 hr.

I) Untreated, acid activated and magnetite nanoparticle loaded bentonite:

Muhammad Ishaq and Siraj Sultan was carried out Adsorptive desulfurization of model oil using untreated, acid activated and magnetite nanoparticle loaded bentonite as adsorbent.Their research work focuses on a novel ultraclean desulfurization process of model oil by the adsorption method using untreated, acid activated and magnetite nanoparticle loaded bentonite as adsorbent. They were used Langmuir and Freundlich isotherm models for analyzing isotherm data Authors was investigated that the bentonite impregnated with magnetite exhibits better performance in the desulfurizationof fuel as compared to bentonite in untreated form as well as activated with HNO3. They were conducted batch experiments for desulphurization process. The adsorption of DBT was also investigated at different adsorbent doses and was found that the percentage adsorption of DBT was increased with increasing the adsorbent dose, while the adsorption in mg/g was decreased with increasing the adsorbent dose. The prepared adsorbents were analyzed by scanning electron microscopy (SEM), energy dispersive X-ray spectrometry (EDX) and X-ray

J) Zn impregnated montmorollonite clay

Adsorptive desulfurization of kerosene and diesel oil by Zn impregnated montmorollonite clay was studied by Waqas Ahmad and Imtiaz Ahmad.Authors carried out research on desulfurization of kerosene and diesel oil has been carried 0.out by selective adsorption through metals impregnated montmorollonite clay. Different metals were impregnated on MMT by wet impregnation method which included Fe, Cr, Ni, Co, Mn, Pb, Zn and Ag. EDX, Surface characterization and SEM analysis of the adsorbents used in the study were conducted to evaluate their mineralogical nature and textural behavior.They showed that the surface area, pore size and pore volume of the MMT has been found to be increased many fold with Zn impregnation. Also the surface morphology of the MMT has also been improved with Zn impregnation. They concluded that Montmorollonite clay can be efficiently used for adsorptive desulfurization and metals impregnation on MMT clay increases its adsorption characteristics.They found that surface area, pore size and pore volume of the MMT was found to be increased many fold with Zn impregnation.

K) Copper supported on zirconia

Desulfurization by adsorption with copper supported on zirconia was studied by P. Baeza ,and G. Aguila. They were used to separate low thiophene concentration from a mixture of 2000 ppmw of thiophene in noctane. Authors was show that the capacity of copper on zirconia to adsorb thiophen increases as the copper content increases, reaching a maximum at a concentration of 3% of copper.[11]The adsorbents were prepared by dry impregnation of zirconium oxide with aqueous solutions of copper nitrate containing the required amount of salt to render Cu concentrations between 1% and 6% for the copper supported on zirconia.The preliminary results presented in this work indicate that samples of Cu supported on zirconia posses a significant adsorption capacity of sulfur-containing compounds, even though the amount of copper of the analyzed samples is relatively low.

L) Mesoporous carbon Adsorbents

Mansoor Anbi, Sajedeh Karami was carried out desulfurization of gasoline using novel mesoporous carbon Adsorbents. They synthesized a novel adsorbent and its adsorption behavior was examined. Ordered mesoporous carbon (OMC) adsorbents have been prepared using spherical SBA-16 mesoporous silica, as a template. The synthesized materials were studied by X-ray diffraction, scanning electron microscopy and nitrogen adsorption–desorption isotherms. Adsorption of dibenzothiophene (DBT) from fuel solution over numerous porous adsorbents such as CMK-3, SBA-15,and OMC has been studied[12].It was concluded that different porous materials considerably have different adsorption capacities towards sulfur removal, which depend not only on the textural structures of the porous materials but also on the surface functional groups. It was found that the amount of DBT adsorption on OMC is higher than SBA16.

M) Copper(II) Modified Bentonite

Desulfurization of Model Oil via Adsorption by Copper(II) Modified Bentonite was studied by Dezhi Yi, Huan Huang, and Li Shi .Authors were showed that modified bentonite adsorbents were effective for adsorption of DMS and PM. The bentonite adsorbents were characterized by X-ray diffraction (XRD) and thermal analysis (TGA). The acidity was measured by FT IR spectroscopy. Several factors that influence the desulfurization capability, including loading and calcinations temperature, were studied. The maximum sulfur adsorption capacity was obtained at a Cu(II) loading of 15wt %, and the optimum calcination temperature was 150 oC. [13]Spectral shifts of the ν(C-S) and ν(Cu-S)vibrations of the complex compound obtained by the reaction of CuCl2 and DMS were measured with the Raman spectrum. Authors were concluded that the characteristic of the Cu-Sand C-S stretching vibrations were found in the Raman spectrum of the Cu(II) complexe. And the FT-IR analyses indicated that the weak Lewis acid sites contributed to the adsorption of sulfur compounds.

III. CONCLUSION

The purpose of this study to show that various types of adsorbent are used for desulphurization of liquid fuels and study of different experiments for construction of adsorption isotherm using different amount of adsorbent in contact with diesel. This paper summerise various adsorbents available for desulphurization techniques.

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